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The ESR spectra of the $\text{Cr}(\text{CN})_6^{3-}$ ion doped into NaCl, KCl, RbCl and KBr hosts

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Abstract. The room temperature ESR spectra of the $\text{Cr}(\text{CN})_6^{3-}$ ion embedded in NaCl, KCl, RbCl and KBr single crystals have been registered. The angular variation of the ESR fine structure was carried out in both the (100) and (110) planes. Several paramagnetic centres were distinguished and characterised by g , E and D spin Hamiltonian parameters. The structure of these centres is discussed in terms of different compensational configurations formed by complex ion and two cationic vacancies. The temperature dependence of the ESR spectra in the 110–300 K range is analysed.

1. Introduction

The spin resonance of paramagnetic impurities is sensitive to their environment and reflects the influence of the nearby defects on the spectral symmetry of the embedded ion. ESR spectra are an excellent and powerful tool for these investigations; therefore studies of the Cr^{3+} ion in a variety of lattices have been performed and discussed in several papers (Jain 1980, Narayama *et al* 1981, Waplak and Stankowski 1969, 1970, 1971, 1974, 1978a, b). The studies of the $\text{Fe}(\text{CN})_6^{3-}$, $\text{Co}(\text{CN})_6^{3-}$ and $\text{Cr}(\text{CN})_6^{3-}$ ions in alkali halides have been carried out by Jain *et al* (1972, 1973), Hanuza *et al* (1984, 1986) and Wang *et al* (1986). Recently there has been considerable interest in the study of alkali halides doped with molecular ion impurities (Narayama *et al* 1981). The chromium(III) ion has a special place among the systems studied because of its laser applications. The possibility of solar collector application (Andrews *et al* 1981) has recently renewed interest in Cr^{3+} ion impurities doped into alkali halide hosts. One of the most important aspects of this problem is the explanation how charge compensating defects and interaction between the trapped ion and compensational vacancies can modify the properties of the active ion. In this paper we report the X-band ESR results obtained in the temperature range 110–300 K for the $\text{Cr}(\text{CN})_6^{3-}$ ion embedded in NaCl, KCl, RbCl and KBr single crystals.

2. Experimental procedures

Single crystals of alkali halides doped with $\text{Cr}(\text{CN})_6^{3-}$ were grown by slow evaporation of a saturated aqueous solution of simple salt containing 1–5% of $\text{K}_3\text{Cr}(\text{CN})_6$ by weight.

The concentration of the complex ion in the host was determined by means of a calibration curve measuring the optical density of the 26600 cm^{-1} peak as a function of the concentration. All chemical operations and storing of the samples were carried out in dark vessels in order to protect the products from hydrolysis or photolysis.

The ESR measurements were performed on a SEX 200 Radiopan spectrometer operating with 100 kHz field modulation. The crystal samples oriented by the x-ray method were mounted in a two-circle goniometer to obtain the angular dependence of the ESR fine structure. The low-temperature studies were made using a liquid nitrogen cryostat manufactured by Kriopan Ltd, Wrocław, Poland.

3. Results and discussion

The ESR spectra of Cr^{3+} ion can be interpreted in terms of the Hamiltonian

$$\mathcal{H} = \beta HgS + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + AS \cdot J$$

where β is the Bohr magneton, H is the applied magnetic field, g is the spectroscopic splitting factor; the effective spin S is $\frac{3}{2}$ for three unpaired electrons, D represents the effect of an initial splitting due to axial symmetry fields, E is the departure from this axial symmetry and the last term represents the interaction between the electron and the magnetic moment of the nucleus with the nuclear spin J . Since the term in A is much smaller than the others, it is omitted in the considerations. The parameters defined here may be determined by studying the angular dependence of the ESR fine structure.

The Cr^{3+} ion, being the paramagnetic impurity in the $S = \frac{3}{2}$ quartet state, exhibits three spin-allowed transitions

$$\Delta M_s = \pm 1: \frac{3}{2} \leftrightarrow \frac{1}{2}, \frac{1}{2} \leftrightarrow -\frac{1}{2} \text{ and } -\frac{1}{2} \leftrightarrow -\frac{3}{2}.$$

The ESR spectra obtained are very complicated since about 30 or more lines are observed for the samples studied. The analysis of such rich spectra was performed by examination of ESR signal anisotropy, i.e. the angular dependence of the fine structure. For that purpose the crystals were rotated in the (100) and (110) planes by an angle of 2.5 degree (figure 1). No hyperfine interaction was observed at room temperature because of the low (9.5%) content of ^{53}Cr nuclei with nuclear spin $\frac{3}{2}$.

The measurements revealed the crystallographical equivalence of the y and z axes. A large number of ESR lines visible in the spectra registered in the two symmetry planes indicated that the spectrum of $\text{Cr}(\text{CN})_6^{3-}$ in alkali halides consists of several overlapping spectra. This confirms the suggestion (Hanuza *et al* 1984, 1986) of the existence of two, or in some cases more than two, different centres in the crystal studied. The analysis of the ESR signal anisotropy allowed us to distinguish two main groups of lines corresponding to two predominant types of differently oriented centres and several weaker lines probably due to the next most important centres.

The centre I corresponds to the configuration formed by $\text{Cr}(\text{CN})_6^{3-}$ and two vacancies nearest to the complex ion along a twofold axis. When two twofold axes and one fourfold axis are the three principal axes of this centre and are parallel to the crystallographic axes, six magnetically inequivalent sites could be distinguished. Since three allowed transitions are possible for each site, 18 fine structure lines could be observed. This number should be reduced to 12 lines when the \vec{H} lies in the (100) and (110) planes. The equivalence of the y and z axes leads to the pairing of the six sites and therefore the number of expected lines should be less than predicted theoretically. Such a situation

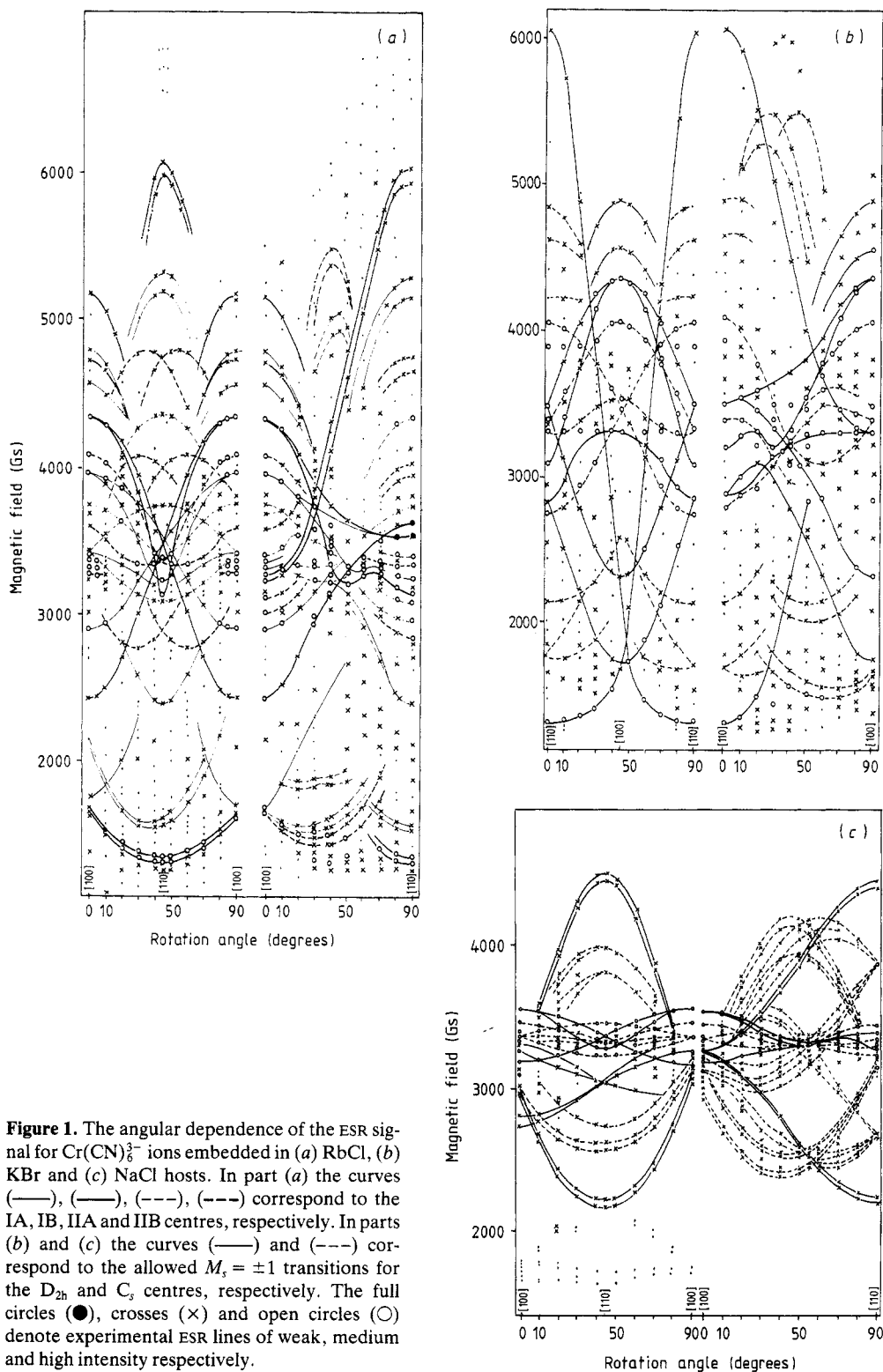


Figure 1. The angular dependence of the ESR signal for $\text{Cr}(\text{CN})_6^{3-}$ ions embedded in (a) RbCl, (b) KBr and (c) NaCl hosts. In part (a) the curves (—), (—), (---), (---) correspond to the IA, IB, IIA and IIB centres, respectively. In parts (b) and (c) the curves (—) and (---) correspond to the allowed $M_s = \pm 1$ transitions for the D_{2h} and C_s centres, respectively. The full circles (●), crosses (×) and open circles (○) denote experimental ESR lines of weak, medium and high intensity respectively.

Table 1. The spin Hamiltonian parameters for $\text{Cr}(\text{CN})_6^{3-}$ in several crystal matrices.

Host	Centre	Lattice constant	g	D (cm^{-1})	E (cm^{-1})	$a = E/D$	Symmetry type
NaCl	I	5.64	1.991 ± 0.003	0.054	0.0165	0.306	D_{2h}
	II		1.994 ± 0.003	0.043	0.006	0.15	C_s
KCl	I	6.28	1.991 ± 0.002	0.091	0.030	0.33	D_{2h}
	II		1.993 ± 0.002	0.071	0.023	0.32	C_s
RbCl	IA	6.59	1.992 ± 0.003	0.093	0.0278	0.299	D_{2h}
	IB		1.992 ± 0.003	0.128	0.040	0.316	D_{2h}
	IC		1.992 ± 0.003	0.165	0.050	0.307	D_{2h}
	ID		1.992 ± 0.003	0.192	0.0576	0.300	D_{2h}
	IIA		1.992 ± 0.003	0.079	0.0238	0.301	C_s
	IIB		1.992 ± 0.003	0.102	0.031	0.308	C_s
	IIC		1.992 ± 0.003	0.129	0.040	0.311	C_s
	IID		1.992 ± 0.003	0.145	0.043	0.300	C_s
KBr	I	6.58	1.991 ± 0.002	0.127	0.042	0.33	D_{2h}
	II		1.994 ± 0.003	0.1015	0.027	0.264	C_s

was analysed and explained (Wang *et al* 1986) as an extremely unusual case in which the axial D and rhombic E distortion parameters have a critical ratio close to $a = E/D = \frac{1}{3}$, where a denotes the non-axiality parameter. All these considerations confirm our conclusion (Hanuza *et al* 1984, 1986) that the centre I has D_{2h} symmetry, which agrees with examinations of Wang *et al* (1986).

The centre II was found to have two principal axes of the crystal-field gradient which do not coincide with the crystallographic axes. They lie approximately in the (100) plane, lying halfway between a twofold and a fourfold axis. Therefore 12 magnetically inequivalent sites are possible, which are paired in a similar way as for centre I (Wang *et al* 1986). The site symmetry of this centre is lower than orthorhombic. The most probable configuration of this centre corresponds to the case when one vacancy occupies a nearest-neighbour site to the complex ion and the other is in a next-nearest-neighbour position. This configuration has C_s symmetry as was proposed by us (Hanuza *et al* 1984, 1986) and others (Wang *et al* 1986).

The centres I and II are present in all the host systems studied. For the KBr and RbCl hosts, besides the above-mentioned two sets of lines and several weak lines corresponding to the forbidden transitions $\Delta M_S = \pm 2, \pm 3$ for centres I and II, the spectra consist of distinct multiplets probably connected with the next centres present in these crystal matrices. The course of these lines for the KBr host is impossible to measure because of their weak intensity, considerably different from those of centres I and II. In addition, these lines disappear in some spectral ranges and orientation of the crystal. The anisotropy of these transitions was determined for the $\text{RbCl}:\text{Cr}(\text{CN})_6^{3-}$ system, where their intensities are more significant. The ESR spectrum of this sample contains the spectral patterns observed both for the KCl and KBr host systems as well as several weak lines in the 1300–1350 Gs region and the over 6100 Gs range. The angular variation of these lines indicates that for the RbCl host eight centres can be distinguished. Four of them have the same orientation as centre I but are characterised by different values of the D and a parameters. These centres we denote as IA, IB, IC and ID, since the respective compensational configurations of the active ion and two vacancies has D_{2h} symmetry. An effect like this may be explained by the assumption that the distance

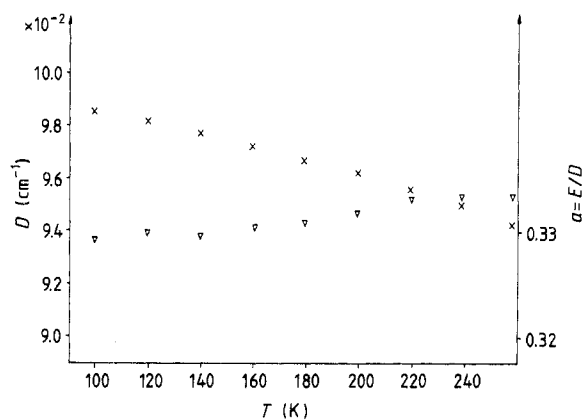


Figure 2. The $D(T)$ and $a(T)$ dependences for $H\parallel z$ measurements of the centre I in the $\text{KCl}:\text{Cr}(\text{CN})_6^{3-}$ system. The crosses (\times) plot the parameter D and the inverted triangles (∇) plot the parameter a .

between the cationic gap and Cr^{3+} ion takes four discrete and different values for the IA–ID centres. It should be noted that the crystal field z axes of the $\text{Cr}(\text{CN})_6^{3-}$ ion in these configurations coincide with $[110]$ direction.

The angular variation of the next set of lines indicates that the remaining four centres have C_s symmetry. Because of their resemblance to the centre II we denote them as IIA–IID. Two of them, IIA and IIC, have their crystal field z axes lying in the (110) plane, but for the remaining centres their crystal field z axes deviate by about 15° from the (110) plane. This is evident from the lines at 2780, 4100 and 4800 Gs, maxima of which appear for the angles 15° and -15° in relation to the $[110]$ plane. The D and a parameters for the centres discussed are listed in table 1.

The centres described here could be characterised by spin Hamiltonian parameters obtained from the (100) and (110) measurements. The $\langle g \rangle$, D and E zero-field splitting parameters were evaluated from the fitting procedure. That procedure was based upon the simulation of the angular dependence of the resonance field for varied $\langle g \rangle$, D and E parameters.

The additional information that supports the assignments presented in table 1 may be obtained from the assumption that the axiality parameter D , characterising the distortion of the $\text{Cr}(\text{CN})_6^{3-}$ octahedron in the host, should be proportional to $1/R^3$, where R is the distance between the central ion and the gap, i.e. the cationic vacancy. The variation of the D parameter for the respective centres in the same host system should produce a relation between the R distances. If we denote the R value for the centre I by R_I (D_{2h} symmetry), this relation for the next centre takes the form $R_{II} = 1.08 R_I$. The sequence of these values coincides with the trend of the series composed from the D parameters of the D_{2h} and C_s centres.

Analysing the results listed in table 1, it should be noted that the $\langle g \rangle$ values are found to be nearly isotropic and respective D and E parameters are close to those reported in the literature (Baker *et al* 1956, Bowers 1952, Wang *et al* 1986). As seen in table 1, the values of the non-axiality parameter $a = E/D$ for centres I and II of the KCl host and centre I of the KBr and RbCl hosts are 0.299–0.316 which is close to $\frac{1}{3}$. This is in agreement with the results obtained by Wang *et al* (1986) and with the experimental course of the $\frac{3}{2} \leftrightarrow \frac{1}{2}$ and $-\frac{1}{2} \leftrightarrow -\frac{3}{2}$ lines, which overlapped accidentally when \vec{H} is swept

in the symmetry planes. In such a case the energy level diagrams are identical for \bar{H} parallel to the z and y axes, although their level sequences are reversed. For the NaCl host and left centres of remaining systems two separate components are visible instead of the degenerate 'double' lines. This is the result of deviation of E/D ratio from $\frac{1}{3}$.

To elucidate the temperature effect on the H_0 resonance field of the centres distinguished, we have measured the angular variation of the fine structure spectra in the 110–293 K temperature range in both the (100) and (110) planes. The temperature behaviour below 220 K results from the deviation of the E/D value from $\frac{1}{3}$. The temperature changes of the D and a parameters for the centre I of the KCl host are presented in figure 2.

The decrease of the temperature leads to the splitting of the 'double' lines of the centre I, an increase of the D parameters for all centres and a decrease of the a parameter. The splitting of the accidentally degenerate lines at RT reaches the value 25 Gs at 110 K.

4. Conclusion

The physicochemical properties of the $\text{Cr}(\text{CN})_6^{3-}$ ion embedded in different alkali halides depend on the nature and lattice dimensions of the host. The properties may be modified by the matrix used. The two cation vacancies created at each $\text{Cr}(\text{CN})_6^{3-}$ centre form two or even more compensational configurations with the complex ion which can be described by D_{2h} and C_s symmetries. The comparison made for ESR line intensities of the centre I and others suggests that number of D_{2h} centres is significantly predominant in all host systems studied. The interaction between the vacancy and the complex ion is considerably compensated by the nearest cyano-ligands. The compensation effect maintains the high symmetry of the CrC_6 polyhedron where the metal ion has octahedral or near octahedral coordination; this is evident from the near isotropy of the g values and non-splitting of $\nu(\text{CrC})$ stretching frequencies (Hanuza *et al* 1989). On the other hand, the stretching structure of the $\nu(\text{CN})$ multiplet is proof that the vacancy-ion compensation effect is held within the limits of cyano-ligand influence. The course and angular anisotropy of the ESR lines suggest that the main distortion axes of the centres created coincide with the [110] direction for D_{2h} and with the [111] direction for C_s centres. The low-temperature ESR signal splitting for the $\frac{3}{2} \leftrightarrow \frac{1}{2}$ lines corresponding to centre I proves the non-axiality of the Cr^{3+} crystal field and its increase as temperature is reduced.

The site constant of the host seems to be the main factor which modifies the properties of the active ion, since its properties are influenced by the space packing of the lattice. For example, the lattice dimensions increase in the series NaCl, KCl, KBr and RbCl. Along the same series we observe a steady increase in the axial D parameter and decreases in the crystal field Δ and vibration frequencies (Hanuza *et al* 1989).

References

- Andrews L J, McCollum B C and Lempicki A 1981 *J. Luminesc.* **24–25** 877
Baker J M, Bleaney B and Bowers K D 1956 *Proc. Phys. Soc. B* **69** 1205
Bowers K D 1952 *Proc. Phys. Soc. A* **65** 860
Hanuza J, Hermanowicz K, Jeżowska-Trzebiatowska B and Wapłak S 1989 *J. Mol. Struct.* in press
Hanuza J, Strek W, Hermanowicz K, Jeżowska-Trzebiatowska B and Trabjerg J 1984 *Chem. Phys.* **86** 137
— 1986 *J. Mol. Struct.* **144** 141

- Jain S C, Warriar A V R and Seghal H K 1972 *J. Phys. C: Solid State Phys.* **5** 1511
— 1973 *J. Phys. C: Solid State Phys.* **6** 193
Jain V K 1980 *Acta Phys. Polon. A* **58** 731
Narayama M, Savasankar V S and Radhakrishna R 1981 *Phys. Stat. Sol.* **105b** 11
Wang D M, Hutton D R and Pikbrow J R 1986 *J. Phys. C: Solid State Phys.* **19** 789
Waplak S and Stankowski J 1969 *Acta Phys. Polon.* **36** 171
— 1970 *Ferroelectr.* **24** 223
— 1971 *Acta Phys. Polon. A* **41** 809
— 1974 *Acta Phys. Polon. A* **46** 175
— 1978a *Acta Phys. Polon. A* **54** 465
— 1978b *J. Phys. Soc. Japan.* **44** 1600